Preliminary note

Second harmonic generation measurements of azobenzene desorption and photochemistry at the interface between an alkane solvent and a glass plate modified with a pyridinium compound

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Abstract

The optical second harmonic generation (SHG) technique was successfully applied to the studies of electrostatic interactions between azobenzene and viologen at the solid/liquid interface. The SHG was compared between an azobenzene-viologen linked compound and non-linked systems. The presence of electrostatic interactions at the interface were verified.　　　© 1998 Elsevier Science S.A. All rights reserved

1. Introduction

Liquid interfaces offer various unique subjects to be probed by the optical second harmonic generation (SHG) technique, such as adsorption/desorption processes of chemical species, chemical reactions, and so on [1]. Azobenzene derivatives may be adequate probe molecules for this purpose, because the photoisomerization induces substantial change in molecular hyperpolarizability. Recently, photoisomerization of azobenzene derivatives have been studied at air/water [2], air/solid [3–10], and liquid/liquid [11] interfaces by using the SHG technique. Most of azobenzene derivatives used for SHG studies have electronically different substituents at 4- and 4'-positions, because they have large molecular hyperpolarizabilities in the *trans*-form ($> 10^{-28}$ esu) due to the contribution of intramolecular charge-transfer effect along the molecular axis. In the case of azobenzene derivatives whose substituents at 4- and 4'-positions are electronically equivalent, on the other hand, molecular hyperpolarizabilities in the *cis*-form should be much larger than those in the *trans*-form. In fact, we found increase in the SHG response from dialkoxyazobenzene adsorbed at the interface between heptane and viologen-modified quartz plate by photoisomerization from *trans*- to *cis*-form. In this study, we demonstrate

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the existence of adsorption/desorption equilibrium of dialkoxyazobenzene photoisomers at the glass/liquid interface.

2. Experimental
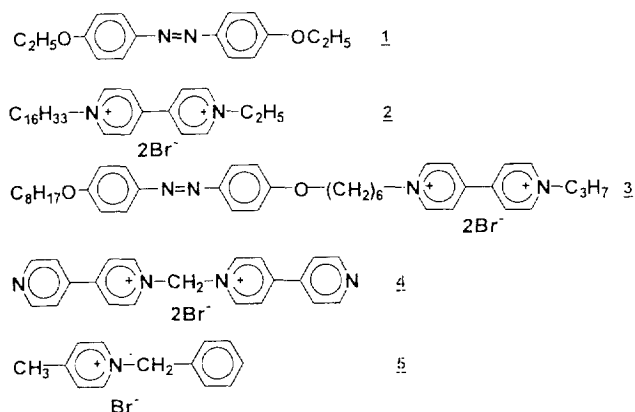
All compounds, 4,4'-diethoxyazobenzene **1**, viologen **2**, an azobenzene–viologen linked compound **3** [12], and pyridium compounds **4** and **5**, were prepared in our laboratory, and their purities were confirmed by elemental analysis and NMR spectroscopy.

A quartz glass plate (8 mm × 40 mm, 1 mm thick) was first treated with KOH-saturated ethanol solution [13,14].

The plate was then kept dipping in methanol solution of **2** $(5 \times 10^{-4}$ M) or a pyridinium compound (**4, 5**) $(1 \times 10^{-4}$ M), or in ethylacetate–methanol (95:5 v/v) solution of **3** $(5 \times 10^{-5}$ M), for 90 min to complete ion exchange, and then dried at room temperature. The electronic absorption spectrum of the modified plate indicated that the surface was covered by a submonolayer of each molecule [15].

In situ SHG measurements were carried out with the modified plate (vide supra) immersed into a heptane solution. The experimental setup for in situ SHG measurements is identical to the one described previously [15]. Briefly, *p*-polarized fundamental light (1064 nm) from a Nd:YAG laser (Continuum YG660B-10S, 5–6 ns, 10 Hz) was incident on the modified plate at various incident angles (θ, see Fig. 1) with respect to the surface normal. The *p*-polarized component of the resultant SHG signal was measured with time-gated detection equipments. Interference patterns of second harmonic waves were clearly observed from the plate, so that the SHG signal was measured by fixing the incident angle at a fringe maximum (around 45°). Photoisomerization of azobenzene was performed by using a high-pressure Hg lamp (500 W), by irradiating a quartz cell (10 mm × 10 mm × 40 mm) perpendicular to the laser beam. The SHG signal was obtained by integrating over 32 laser pulses. Thus time response of the system is 4–5 s.

Two types of photoisomerization—SHG experiments were carried out as shown in Fig. 1. In Fig. 1a, 1 ml of the heptane solution (or heptane) was added in the quartz cell together with the modified plate, and the entire region of the solution was irradiated by the Hg lamp to perform photoisomerization in the whole solution. In contrast, 2 ml of the heptane solution (or heptane) was added in the quartz cell and only a partial region (2 mm × 10 mm × 10 mm) of the solution was irradiated. In both cases the laser was introduced at the middle position of the irradiation region by the Hg lamp.

3. Results and discussion

The isomer ratio of **1** in heptane was adjusted by irradiating light from the Hg lamp. The *trans*-to-*cis* isomerization was induced by ultraviolet light from the Hg lamp up to 340 nm (denoted by Sw), while *cis*-to-*trans* isomerization by visible light above 400 nm (denoted by Lw). In the case of a heptane solution of **1** $(2 \times 10^{-4}$ M), the isomer ratio (*trans* vs. *cis*) was kept constant even by repeated Sw–Lw irradiation cycles: 26 vs. 74% for Sw irradiation, and 72 vs. 28% for Lw irradiation. These ratios were retained more than 30 min in the dark. Before irradiation, **1** was present as the *trans*-form quantitatively.

The SHG response at a fixed incident angle was continuously recorded during Sw (1 min)–dark (2 min)–Lw (1 min) irradiation cycles of the entire region (Fig. 1a). Fig. 2a shows variation of SHG signals with the irradiation cycles.
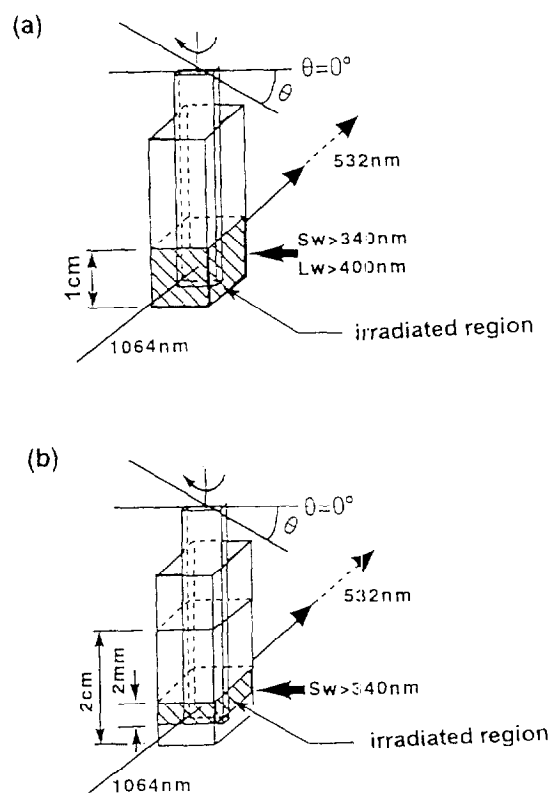

Fig. 1. Experimental geometries for photoisomerization—SHG measurements. The high-pressure Hg lamp irradiated the entire region (a) or a partial region (b) of the solution at a right angle from the laser beam.
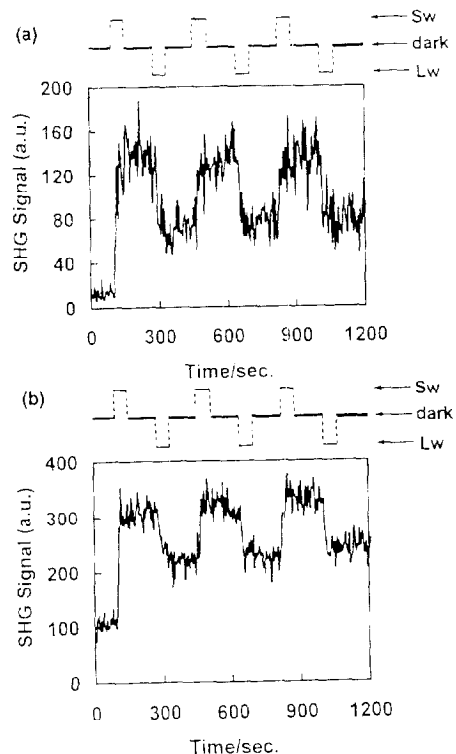

Fig. 2. Variations of SHG signals on photoisomerization of azobenzene: (a) **2**-modified plate in the heptane solution of **1** $(2 \times 10^{-4}$ M), (b) **3**-modified plate in heptane. The SHG signal at a fringe maxima (around 45°) was recorded during Sw–dark–Lw irradiation cycles. The irradiation scheme is shown on the top of the figure.

when the 2-modified plate is immersed into the heptane solution of **1** (2 × 10⁻⁴ M). Before irradiation, the SHG signal was very small because the content of *cis*-isomer is negligible. The signal increased steeply with the first Sw irradiation because the majority (74%) of **1** in the whole solution converted to the *cis*-isomer, and remained constant in the subsequent dark period. Then, the signal decreased by the subsequent Lw irradiation due to the decrease of *cis*-isomer from 74% to 28%. Repeated Sw–dark–Lw irradiation gave reproducible changes of SHG signals. Previous results indicated that the SHG response was ascribed to noncentrosymmetric alignment of SHG-active *cis*-isomer of a 4,4′-dialkoxyazobenzene on the 2-modified surface due to interactions between viologen- and 4,4′-dialkoxyazobenzene moieties. If the intramolecular charge-transfer interaction from the ethoxy unit to the azo unit is assumed to induce the molecular hyperpolarizability (β) in 4,4′-dialkoxyazobenzene, β-values for *cis*- and *trans*-isomers are estimated to be the orders of 10⁻³⁰ esu and 10⁻³² esu, respectively, by molecular orbital calculation.

In a similar manner, the SHG response was investigated when the glass plate modified with azobenzene–viologen linked compound **3** was immersed into heptane. As shown in Fig. 2b, the signal was ca. 100 (arbitrary units) before irradiation. The signal increased substantially by the Sw-irradiation, and the subsequent signal changes with Sw–dark–Lw irradiation cycles were quite reproducible. In each Sw–dark–Lw irradiation cycle the signal in Fig. 2b was larger as compared with the corresponding signal in Fig. 2a.

When a part of the heptane solution (or heptane) was irradiated by the Sw light for 8 s as shown in Fig. 1b, quite different SHG profiles from Fig. 2 were observed. In the case of 2-modified plate immersed into the heptane solution of **1**, the SHG signal increased concomitantly with Sw-irradiation, but decreased with time after ceasing photoirradiation (Fig. 3a). In the case of 3-modified plate immersed into heptane, on the other hand, the SHG signal increased similarly by Sw-irradiation, but it was retained more than 100 s even after ceasing photoirradiation (Fig. 3b). These results clearly indicate the existence of adsorption/desorption equilibrium of **1** at the 2-modified surface. During Sw-irradiation for 8 s, some of **1** convert to the *cis*-isomer responsible to SHG. The formed *cis*-isomer in the photoirradiated region, however, diffuses away into the non-irradiated bulk region. In fact, the SHG signal level in the dark period increased gradually by repeating Sw (8 s)-irradiation, due to gradual increase of the *cis*-isomer in the solution. In the case of azobenzene–viologen linked compound **3**, however, the azobenzene moiety cannot diffuse away from the viologen-modified surface, so that the SHG signal is retained even after ceasing partial photoirradiation.

For both irradiation geometries, the SHG signal from the 3-modified plate in heptane was larger than the corresponding signal from the 2-modified plate in the heptane solution of **1**. According to absorption spectral measurements, amounts of **2** and **3** on the plates were comparable. These results are
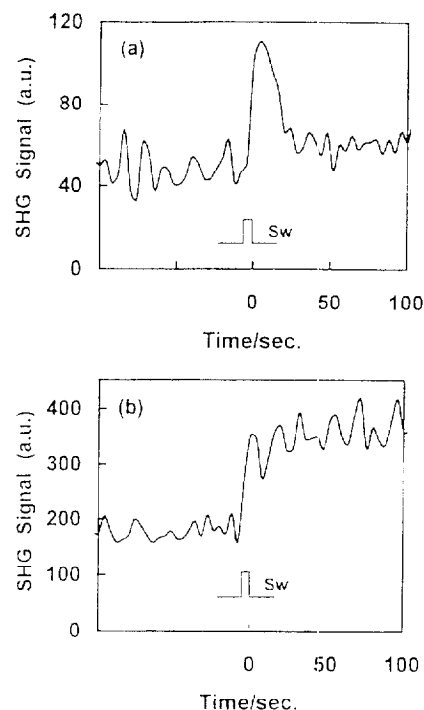
consistent with the existence of adsorption/desorption equilibrium in the case of non-linked azobenzene and viologen system.

Partial irradiation experiments by the Sw light (8 s) were also carried out for the 4-modified plate (vide infra) in the alkane solution of **1** (2 × 10⁻⁴ M). As shown in Fig. 4, the SHG signal increased with Sw-irradiation in each alkane solution. However, the decay time of the SHG signal after ceasing photoirradiation was shorter for the solvent with

Fig. 3. Time profiles of SHG signal changes due to a partial irradiation of the solution by Sw light (<340 nm) for 8 s: (a) 2-modified plate in the heptane solution of **1** (2 × 10⁻⁴ M). (b) 3-modified plate in heptane. The Sw-irradiation condition is shown in the figure.
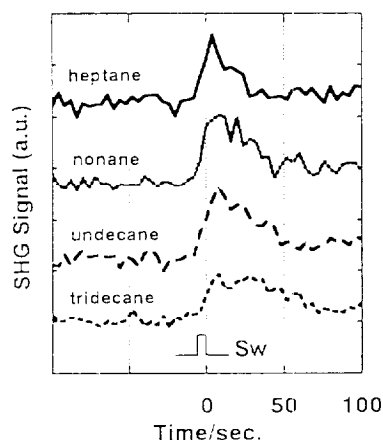

Fig. 4. Effects of alkane solvents on the decay profiles of SHG signals after ceasing Sw-irradiation (8 s) of the partial region of the alkane solution containing **1** (2 × 10⁻⁴ M). The 4-modified plate is used. The Sw-irradiation condition is shown in the figure.

lower viscosity: half-widths of the signal profiles are ~ 15 s for heptane (viscosity (mPa s) at 20–23.3°: 0.41), ~ 28 s for nonane (0.71), ~ 32 s for undecane (1.17), and ~ 49 s for tridecane (1.55). These observations are consistent with the results of Figs. 2 and 3; molecular diffusion is slower for a solvent with higher viscosity so that the noncentrosymmetric alignment of the *cis*-isomer can be retained for a longer time in a more viscous solvent.

In order to elucidate the role of viologen moiety on the glass surface for obtaining the SHG response from the *cis*-isomer, some other pyridinium compounds **4** and **5** were used in stead of viologen. The intensities of SHG signals from the modified plates with **2**, **4**, and **5** were compared in the heptane solution of **1** $(2 \times 10^{-4}$ M) at the first Sw-irradiation. Although the surface coverages of **2** and **4** were comparable each other, the signal from **4**-modified plate was about twice as large as that from **2**-modified plate; thus, the **4**-modified plate was used in the study of viscosity effect (Fig. 4) to improve the signal-to-noise ratio. In the case of **5**-modified plate, the surface coverage was more than twice those of **2** and **4**, but the SHG signal was negligibly small. These results imply that the electrostatic interaction between the pyridinium groups of **4** and the oxygen atoms of dialkoxyazobenzene **1** occurs more snugly than in the case of **2**. Probably the cationic pyridinium moieties of **2** and **4** are more exposed to the heptane solution as compared with the pyridinium group of **5**; the hydrophobic benzil group of **5** may be stand-up from the glass surface so as to hinder the electrostatic interaction described above.

In the previous spectroscopic studies of the azobenzene–viologen linked compounds, no appreciable interactions between azobenzene and viologen moieties have been reported in bilayer membranes [12]. The present in situ SHG results clearly indicate the presence of electrostatic interactions between the two moieties at the glass/solution interface when the viologen moiety is confined at the glass surface.

Detailed studies as to the role of spatial alignments for cationic moieties on the plate are now in progress.

Acknowledgements

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